Chapter 12
Biomass to Liquid Fuel via Fischer–Tropsch and Related Syntheses

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Abstract This chapter briefly reviews the state of art on the conversion of biomass to biofuels by gasification followed by the gas to liquid conversion of biosyngas via Fischer–Tropsch and related syntheses. An integrated process to produce heat, electricity, or fuel by gasification and Fischer–Tropsch synthesis is analyzed. The present state of gasification reactor technology is outlined. The strategies for syn-gas cleanup are delineated. The catalysis and processes for methanol, Fischer–Tropsch, and isosynthesis are briefly evaluated. Finally, various approaches to an integrated process design depending on the desired end results (heat, electricity, or fuel) and the associated economics for each approach are outlined and briefly discussed.

1 Introduction

The world energy demand is increasing at a faster rate than its supply. This is particularly true for the transportation fuel. The sources for total world energy supply at the present time are graphically illustrated in Fig. 1. It is clear from this graph that coal and renewable sources combine to provide as much energy as oil. Heat, electricity, and transportation fuel are the major forms of energy use. While heat and electricity are derived from all sources of energy, transportation fuel has been largely obtained from the oil and natural gas. Although the major world reserve of crudes, heavy oils, and natural gas reside in regions like Middle East, Canada, Venezuela, Russia, etc., the United States is the largest consumer of these forms of energy. In fact, because of the supply and demand discrepancies for the United States, more than 60% of oil consumed by the United States is imported from the foreign countries. Furthermore, the global supply of oil is decreasing, while the demand is increasing. One of the reasons

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J.W. Lee (ed.), *Advanced Biofuels and Bioproducts*, DOI 10.1007/978-1-4614-3348-4_12,
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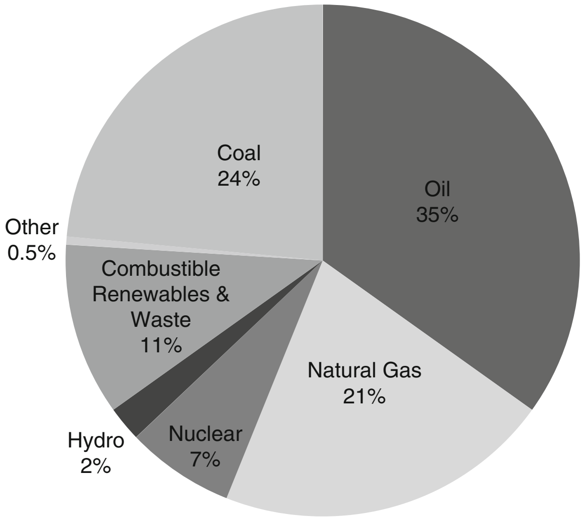


Fig. 1 Total world primary energy supply (after Olah et al. [3])

for this is the aggressive economic development and the resulting energy need by the countries such as China, India, Latin America, and Russia among others [1, 2].

It is imperative for the United States to be less dependent on foreign oil and develop alternate domestic sources to produce power for heat and electricity and synthetic oils. Besides crude oil and natural gas, the United States also uses considerable amount of coal, particularly for the power industries. The United States has the largest reserve of coal (which can last up to 200 years) [1, 2], which can also be a very good oil substitute for the production of transportation fuels. This can decrease the U.S. dependence on the foreign crude and heavy oil significantly. The technologies that have the most promise to convert coal to heat and electricity and/or liquid fuel include coal pyrolysis, combustion, and gasification. Gasification converts coal into producer gas with different amounts of methane, depending upon the gasification technology. The producer gas can either be used for heat and electricity or it can be converted into syngas (which largely contains CO and H_2) by reforming technology. The syngas can then be converted to a liquid fuel by means of Fischer–Tropsch (FT) synthesis. Both coal-based power production and CTL (coal-to-liquid) technology are commercially available. Unfortunately, they suffer from unacceptable production of green house gases (GHG) such as carbon dioxide and other harmful volatile organic compounds. While other toxic compounds can be removed from power generation and CTL plants, the sequestration of carbon dioxide still remains a major issue.

While for the past several decades the use of biomass for the source of heat, electricity, and transportation fuel has been extensively examined in Europe, Brazil, and several other countries, in recent years the use of biomass as a raw material for heat and electricity and transportation fuels is also becoming increasingly important in the United States. The energy available from renewable biomass sources in the United States has been estimated to be about 20% of the U.S. energy consumption [1, 2]. There are basically three classes of feedstocks derived from biomass that are appropriate for the production of renewable fuels for heat, electricity, and transportation fuel: (1) starchy and edible feedstocks such as corn, beets, sugar cane, (2) triglyceride feedstocks such as soybeans, algae, jatropha, and about 350 other types of crop oils, and (3) lignocellulosic feedstocks. While, bioethanol and biodiesel derived from first two sources are commercialized and continue to be examined, it is the lignocellulosic biomass that is the most abundant class of biomass. While starch and triglycerides are only present in some crops, lignocellulose contributes structural integrity to plants and thus always present. In general, most energy crops and waste biomass, such as switch grass, miscanthus, agricultural residues, municipal wastes, animal wastes, waste from wood processing, waste from paper and pulp industries, etc., are lignocellulose that can be used for the generation of heat, electricity, and transportation fuel. The analysis carried out by EPA [4] shows that the use of biomass fuel sources results in the generation of significantly lower quantities of anthropogenic CO_2 emissions during power or fuel productions.

Biomass can be converted to biofuels in a number of different ways. For lignocellulosic biomass, thermochemical methods for the productions of biosyngas and bioliquids are very popular. These methods utilize gasification, reforming, pyrolysis, extraction, and liquefaction technologies to convert biomass into a variety of biogas and bioliquids. One method widely used is the gasification of biomass followed by reforming and gas cleaning to produce clean syngas. This syngas can be converted to a variety of bioliquids via well-known FT and related syntheses. This method is very versatile in that it can generate biofuels for heat, electricity, or transportation as well as for chemical feed stock. This brief chapter addresses three aspects of this method of biomass conversion: (a) basic chemistry and catalysis of FT and related processes for the conversion of biosyngas to bioliquids, (b) brief descriptions of various processes that currently exist for biomass to biosyngas and biosyngas to methanol and transportation fuels via FT and related syntheses, and (c) a brief assessment of an integrated process for the conversion of biomass to synthetic biodiesel fuel.

2 Fundamentals of Fischer–Tropsch and Related Chemistry and Catalysis

The general reactions for the hydrogenation of carbon monoxide are given as:

$$(2n+1)\mathrm{H}_2 + n\mathrm{CO} = \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H}_2\mathrm{O} \tag{1}$$

$$(n+1)\mathrm{H}_2 + 2n\mathrm{CO} = \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{CO}_2 \tag{2}$$

$$2n\mathrm{H}_2 + n\mathrm{CO} = \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H}_2\mathrm{O} \tag{3}$$

$$n\mathrm{H}_2 + 2n\mathrm{CO} = \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{CO}_2 \tag{4}$$

$$2n\mathrm{H}_2 + n\mathrm{CO} = \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{H}_2\mathrm{O} \tag{5}$$

$$(n+1)\mathrm{H}_2 + (2n-1)\mathrm{CO} = \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{CO}_2 \tag{6}$$

Table 1 Influence of temperature and pressure on equilibrium conversion in a typical synthesis reaction: $20H_2 + 10CO = C_{10}H_{20} + 10H_2O$ (conversion = 80%) (after Anderson [5])

Temp. (°C)	Pressure atm abs
300	1
390	10
420	20
445	30
475	50

These reactions represent the formation of paraffins, monoolefins, and alcohols. The reactions generate water or carbon dioxide as by-products. As the concentration of carbon monoxide compared to that of hydrogen is increased, by-products change from water to carbon dioxide. However, the desired product can still be obtained during this change in the formation of the by-product.

Since the synthesis reactions lead to a smaller number of gaseous molecules, the equilibrium conversion at any given temperature increases with pressure. The influence of temperature and pressure on equilibrium conversion of reaction (3) is given in Table 1. As given in the table, for the formation of 1-decene (reaction (3)), an increase in pressure by 50 atm allows temperature to be increased by 175°C to obtain the same level of conversion.

Generally, the reactions forming carbon dioxide rather than water have larger equilibrium constants. The standard free energy per carbon atoms, $\Delta F^o/n$, for reactions producing methane is more negative than that of the reactions forming the higher hydrocarbons. In addition, the free energy of elemental carbon formation is more negative than that for the higher hydrocarbons; therefore, the production of higher hydrocarbons for liquid fuels must depend on the selectivity of the catalyst. The nature of the catalyst affects the Schultz-Flory chain growth distribution of FT products [6]. Also, as given in Table 2, different catalysts and promoters under various temperature and pressure conditions produce varying products from the reactions between carbon dioxide and hydrogen [8]. Three most commercialized reactions in Table 2 are methanol synthesis, FT synthesis, and isosynthesis. The last synthesis converts syngas into branched hydrocarbons. We will mainly focus our discussion on these three syntheses.

2.1 Methanol Synthesis

Methanol synthesis has been postulated to occur via two different types of reaction steps. One mechanistic view indicate methanol to be formed by direct reaction (7) between carbon monoxide and hydrogen as:

$$CO + 2H_2 = CH_3OH \tag{7}$$

Table 2 Products of reaction between carbon monoxide and hydrogen [7]

	Catalysts	Promoters	Temp. (°C)	Pressure (atm)	Product
Methane synthesis	Ru		250–500	1	Chiefly methane
	Ni	ThO_2, MgO	250–500	1	Chiefly methane
Fischer–Tropsch synthesis	Fe, Co, Ni	ThO_2, MgO, Al_2O_3, K_2O	150–350	1–30	Paraffinic and olefinic hydrocarbons up to waxes, plus small to large quantities of oxygenated products
	Ru		150–250	100–1,000	High molecular weight paraffinic hydrocarbons
Methanol synthesis	ZnO, Cu, Cr_2O_3, MnO		200–400	100–1,000	Methanol
Higher alcohol synthesis	Same as in C	Alkali	300–450	100–400	Methanol and higher alcohols
Isosynthesis	ThO_2, $ZnO + Al_2O_3$	K_2O	400–500	100–1,000	Saturated branched hydrocarbons
Oxosynthesis[a]	CO, Fe		100–200	100–200	Oxygenated organic compounds

[a] This reaction involves hydrogen, carbon monoxide, and olefins

Also,

$$CO_2 + H_2 = CO + H_2O \tag{8}$$

Thus, in this view, methanol is predominantly synthesized via direct hydrogenation of carbon monoxide (reaction (7)). The second reaction (8) is a reverse water gas shift (WGS) reaction. Experimental data containing 3–9% carbon dioxide in feed show a decrease in carbon dioxide concentration in the effluent stream indicating the presence of the second reaction. The first reaction (7) is exothermic, while the second reaction (8) is endothermic. In this mechanism, the presence of carbon dioxide in the feed is extremely important. Low carbon dioxide in the feed will result in lower methanol productivity. Typically, 2–4% of carbon dioxide is present in the syngas mixture for the vapor phase synthesis of methanol and the corresponding value for the liquid phase methanol synthesis is 4–8% [9, 10].

The second view implies that the principal chemical reactions that lead to the synthesis of methanol are [9–13]:

$$CO_2 + 3H_2 = CH_3OH + H_2O \tag{9}$$

$$CO + H_2O = CO_2 + H_2 \tag{10}$$

According to this view, the synthesis of methanol proceeds predominantly via direct hydrogenation of carbon dioxide and WGS reaction proceeds in the forward

Table 3 Commercial processes for methanol synthesis (after Lee et al. [14])

Process	Comments
The conventional ICI's 100 atm methanol process	$Cu/ZnO/Al_2O_3$ catalyst system; two parts: reforming and synthesis gas conversion
Haldor Topsoe A/S low pressure methanol process	Low capital cost; two stage reforming; suitable for smaller and larger plants (10,000 tons per day)
Kvaerner methanol process	Similar to Haldor Topsoe process; CO_2 can be used as supplementary feed; 2,000–3,000 mtpd typical size
Krupp Uhde's methanol process	Flexible feedstock, different steam reforming; at least 11 plants
Lurgi Ol-Gas-Chemie GMBH process	10,000 mtpd capacity; two stage reforming
Synetix LPM process	Large capacities; improved ICI's LPM
Liquid phase methanol process	Three stages developed by Chem Systems Inc.; slurry reactor; $Cu/ZnO/Al_2O_3$ catalyst at 230–260°C, 50–100 atm

direction. The WGS reaction produces carbon dioxide which in turn increases the productivity of the methanol production. A significant literature is available to justify each of these two mechanistic views for the methanol productions.

Numerous commercial processes for methanol synthesis are available. These processes have exploited both high and low pressure operations as well as both vapor phase and liquid phase operations. Some of the important commercial processes are outlined in Table 3. The details of these processes are given by Lee et al. [14].

2.2 FT Synthesis

The FT synthesis process can be made generally selective by proper choice of operating conditions and catalysts. Most of the studies over last several decades have been focused in this area. The status of the several FT processes through 1950 is given in Table 4. The yield of C_3^+ product per cubic meter of synthesis gas given in this table is very important because it directly relates to the purity of the synthesis gas. The cost of the production of purified synthesis gas can be as high as 70% of the total cost of the FT process [16]. Earlier work focused on Fe catalysts and the improvements in these catalysts that would increase their operability and selectivity and decrease the operating costs of FT process [16]. The efforts were made to prevent the reaction $2CO = CO_2 + C$ and improve the steady-state life of the catalyst. Significant developmental efforts were also made [17, 18] for a more active and mechanically stable catalyst to further reduce the yields of C_1 and C_2 [19]. The process improvement efforts were also focused on developing a catalyst which minimized the shift reaction.

It was suggested [8] that further selectivity in FT reactions can be attained by either poisoning acceptable catalysts with sulfur compounds or by selecting sulfides of less frequently used catalysts. Storch et al. [20] reported that the initial effect of small amounts of H_2S is the increase in nickel–manganese catalyst activity. This was also confirmed by Herrington and Woodward [21] for cobalt–thoria–kisselguhr

Table 4 Characteristics of various Fischer–Tropsch processes [15]

Catalyst	Temp. (°C)	Pressure (atm)	C_3^+, (g/m^3)	C_3^+,[a] (kg/m^3)	Gasoline[b]	Diesel[b]	H.O. + wax	Water-soluble chemicals[b]	Steel,[c] tons/(bbl day)	Motor octane number[d]	Cetane number
Granular catalyst, externally cooled, no gas recycle											
CO	175–200	1	140	8	56	33	11	[e]	2.7	50	100
CO	175–200	10	150	10	35	35	30	[e]	2.4	25	100
Fe	200–225	10	125	10	32	18	35	15	2.5	…	…
Granular catalyst, externally cooled, gas recycle											
CO	190–224	10	160	13	50	22	22	8	1.9	…	…
Fe	230	20	145	14	19	19	58	8	2.1	…	…
Fe	275	20	145	11	68	19	3	8	2.2	…	…
Powdered catalyst, oil slurry, gas recycle											
Fe	250–275	20	170	20	25	30	31	4	1.2	…	…
Granular catalyst, internally cooled, gas recycle											
Fe	240–280	20	170	58	58	10	24	8	0.7	74	78
Granular catalyst, hot-gas recycle											
Fe	300–320	20	140	32	70	17	1	12	0.7	75	50
Fluidized catalyst, gas recycle											
Fe	300–320	20	150	115	73	7	3	17	0.6	76	…

[a] Kilogram of total product, excluding water, carbon dioxide, methane, ethane, and ethylene per volume of reactor per unit time

[b] Weight percent of oil plus water-soluble product

[c] In converter and its accessories only

[d] Bauxite treated, but no T.F.L. added

[e] Very small, less than 1%

(100:18:100) catalysts. In their experiments, H_2S is mixed with the synthesis gas in small batches and no H_2S was eliminated in the off-gas during the course of sulfur poisoning experiments. The first addition of H_2S increased the yield of liquid hydrocarbons at constant temperature. As sulfur addition continued, there was a decrease in the yield of gaseous hydrocarbons. Total hydrocarbon yield increased with sulfur addition to the catalyst until 8 mg. of sulfur was added to each gram of catalyst. This work suggested the advantage of stopping sulfidization at low level (1–4 mg of sulfur/g of catalyst) to obtain the benefits of increased liquid hydrocarbons yield. The results also suggested that the catalyst might show the same behavior if presulfided to the same degree before introducing the synthesis gas. The patent of Storch et al. [22] showed that 69% of CO conversion can be obtained for a molybdenum disulfide catalyst alkalized with 2–3% KOH in a feed of $2H_2 + CO$ at 530°F and 13.6 atm. Products from this synthesis were low boiling with 30% of the product C_3^+ hydrocarbons and organic oxygenated compounds. Laynes [23] indicated that by allowing the sulfur content of the iron catalyst to build up to an optimum ratio and maintain at that level will minimize CO_2 formation during hydrogenation of CO to form hydrocarbons.

Over last several decades, a continuous effort to improve catalyst activity, selectivity, and stability has been carried out. Besides looking at different forms of iron catalysts, nickel, cobalt, and ruthenium catalysts have been extensively studied. Both cobalt and ruthenium catalysts with different types of promoters have been extensively examined by Exxon and other oil companies. Their studies indicate that while these catalysts give higher initial activity, they also tend to decay rapidly. Numerous patents on these catalysts have been reported by Exxon and other oil companies. In recent years, MOF (metal organic framework) have been tested to improve the selectivity of FT reactions. This work is being carried out at NETL in Pittsburgh and it is still at the development stage. More work in this area (perhaps using recent developments in nanotechnology) is needed.

2.3 Isosynthesis

Isosynthesis (for the production of branched hydrocarbons) is interesting because (a) under proper conditions it gives saturated branched-chain aliphatic hydrocarbons containing 4–8 carbon atoms, (b) compared to other types of synthesis, it is the only one that uses difficult reducible oxides as catalysts [24–27], and (c) it produces isobutane for high octane gasoline. The oxide catalysts that are used for this synthesis are thorium oxide, aluminum oxide, tungstic oxide, uranium oxide, and zinc oxide. The thoria and alumina catalysts can be prepared by precipitation from nitrate solutions by adding a hot sodium carbonate solution. The other oxide catalysts can be prepared by addition of alkali to their respective nitrate solutions except in the case of tungsten which can be precipitated from Na_2WO_4 solution by nitric acid addition.

The most effective catalysts for isosynthesis are the tetravalent oxides, thoria, ceria, and zirconia. Alumina and the other oxides are not as effective in producing

Table 5 Isosynthesis results over one-component catalysts (450°C, water gas conversion [28])

Catalyst	Water gas conversion 30 atm	150 atm	300 atm	% Hydrocarbons	C no.	% i-C_4 in C_4 fraction
Thoria[a]	19			2.1	2.1	
Thoria		46		5.1	2.6	88
Thoria			66	6.4	2.8	
Alumina[b]	54			11.0	1.4	
Alumina[b]		53		10.5	1.5	59
Alumina[a]			21	3.1	2.0	
W_2O_5	58			12.9	1.3	
ZrO_2[a]	9			1.0		
ZrO_2		31		3.5	2.1	82
ZrO_2			36	3.5	2.3	
UO_2[a]				3.7	1.4	
ZnO[a]	10			1.2	1.3	
ZnO			44	10.0	1.1	
CeO_2[a]	7			0.5	2.0	
CeO_2		10		1.0	2.4	81

[a] From nitrates

[b] From sodium aluminate (or tungstates)

isobutane. Other oxides such as chromia, lanthana, praseodymium oxide, magnesia, manganese oxide, titania, and berylia have been tested but they had lower activity. Of all the catalysts tested so far, thoria or promoted thoria has been the most promising catalysts. Unlike catalysts of iron group, thoria is not poisoned by sulfur compounds. In addition, an activity decline due to carbon deposition can be easily overcome by simply passing air over the catalyst to generate CO_2 at the synthesis temperature. Some typical results for one-component catalysts at various pressures are given in Table 5.

Thoria catalyzes the production of hydrocarbons with relatively high carbon number from synthesis gas. Furthermore, the so-called gasol hydrocarbons consisting of mainly C_3–C_4 also contain large amounts of isobutane. In contrast, the trivalent oxide alumina produced mainly methane and carbon with small amount of “gasol” and traces of isobutane. The most active divalent oxide, zinc oxide, produced no liquid hydrocarbons but mainly methane and alcohols. For thoria catalyst, the best temperature has been found to be between 375 and 475°C. Alcohol production dominated below 375°C and methane and LPG were the main products between pressure of 300 and 600 atm. Below 300 atm, gas conversion was small; above 600 atm, methane and dimethyl ether were obtained.

The effects of additions of various promoters on the performance of thoria catalysts have also been examined. Three promoters have been studied: (1) alkali to increase molecular weight of the product, (2) phosphoric acid to convert unsaturated hydrocarbons such as propane to *n*-butene to higher branched hydrocarbons particularly to dimers, and (3) zinc oxide and alumina to enhance the formation of alcohols and subsequently the dehydration of alcohols for the formation of branched hydrocarbons.

The alkali did not work well and the activity of thoria catalyst decreased with an increase in alkali content. The most effective promoter was alumina. For thoria–alumina catalyst, the literature data show [29] that the amount of isobutene increased with an addition of alumina; best results were obtained at 20% alumina on thorium oxide. Catalysts prepared by separate precipitation and mixing of the wet precipitates produced the highest i-C_4 (isobutane) yields. While "gasol" increased with an increase in temperature, C_5^+ and alcohols (not shown in the table) decreased with an increase in temperature. i-C_4 increased with an increase in temperature. In this study, thoria was precipitated from a nitrate solution with sodium carbonate while aluminum oxide was precipitated from a sodium aluminate solution using sulfuric acid. Finally, the best thoria–alumina–zinc oxide catalysts gave lower yields of isobutane and somewhat higher yield of C_5^+ hydrocarbons than thoria–alumina catalysts. Once again, just like for FT synthesis, most recent efforts on the catalyst development for isosynthesis are focused on improving product selectivity.

3 Processes for Syngas Productions and Syngas to Liquid Conversion

A process for converting fossil fuels such as crude oil, heavy oil, coal, shale oil, tar sand, bitumen, etc., or biomass to liquid fuels such as methanol, biogasoline, biodiesel, or biojet fuel, etc., generally contain five steps: pretreatment, gasification, gas cleaning and conditioning, FT process, and final product separation and possible upgrading. This section outlines some details of each of these steps with special attention to biomass feedstock.

3.1 Pretreatment

The first step is the pretreatment of fossil fuel or biomass. Here undesired impurities such as mineral matters, inorganic impurities (particularly in biomass), sulfur, etc., are removed and particle size of the feed stock is adjusted to satisfy the need of the subsequent gasification process. Pretreatment of coal requires removal of ash and sulfur along with adjustment of the particle size. The inorganic sulfur and ash are often removed by the floatation technique supported by the fine particle technology. Pretreatment step is particularly important for biomass. Unlike coal, biomass is a low density (both mass and energy) product and easily degradable in the natural environment. The storage and transportation of biomass are very problematic because of its low density and easy degradation. The reduction of biomass particle size to the desired level is also problematic because it requires high grinding energy. Biomass is generally wet and contains a large amount of water. The removal of this water is also important for high energy efficiency of the gasifier.

Numerous pretreatment processes for biomass have been examined. The advantages and disadvantages of these processes are outlined in Table 6.

Table 6 Summary of advantages and disadvantages of various biomass pretreatments [30]

Biomass pretreatment	Advantages	Disadvantages
Sizing (grinding, chipping, chunking, milling)	Adjusts the feedstock to the size requirement of the downstream use	Nonbrittle character of biomass creates problems for sizing Should be done before transportation but storage of sized materials increases dry matter losses and microbiological activities leading to GHG (CH_4, N_2O) emissions
Drying	Reduces dry matter losses, decomposition, self-ignition, and fungi developments during storage Increases potential energy input for steam generation	Natural drying is weather dependent; drying in dryers requires sizing
Bailing	Better for storage and transportation; higher density and lower moisture content	Cannot be used without sizing for gasification
Briquetting	Higher energy density, possibility for more efficient transport and storage Possibility for utilization of coal infrastructure for storage, milling, and feeding; rate of combustion comparable with coal Reduces spontaneous combustion	Easy moisture uptake leading to biological degradation and losses of structure Require special storage conditions Hydrophobic agents can be added to briquetting process, but these increase their costs significantly
Washing/leaching	Reduction of corrosion, slagging, fouling, sintering, and agglomeration of the bed washing is especially important in case of herbaceous feedstock Reduced wearing out of equipment, and system shut down risks	Increased moisture content of biomass Addition of dolomite or kaolin, which increases ash melting point, can also reduce negative effects of alkali compounds
Pelletizing	Higher energy density leads to better transportation, storage and grinding, and reduced health risks Possible utilization of coal infrastructure for feeding and milling (permits automatic handling and feeding)	Sensitive to mechanical damaging and can absorb moisture and swell, loose shape, and consistency Demanding with regard to storage conditions

(continued)

Table 6 (continued)

Biomass pretreatment	Advantages	Disadvantages
Torrefaction	Possibility for utilization of coal infrastructure for feeding and milling Improved hydrophobic nature—easy and safe storage, biological degradation almost impossible Improved grinding properties resulting in reduction of power consumption during sizing Increased uniformity and durability	No commercial process Torrefied biomass has low volumetric energy density
TOP process	Combines the advantages of torrefaction and pelletizing Better volumetric energy density leading to better storage and cheaper transportation Desired production capacity can be established with smaller equipment Easy utilization of coal infrastructure for feeding and milling	No commercial process Does not address the problems related to biomass chemical properties, i.e., corrosion, slagging, fouling, sintering, or agglomeration

For combustion and gasification, biomass particle size, water content, decay resistance, and inorganic impurities are important parameters. For these reasons, leaching and torrefaction are considered to be the two most important pretreatment steps. Leaching process will remove salts and other inorganic impurities from the biomass and can be easily carried out using hot water or steam. Torrefaction process makes biomass hydrophobic, easy to crush, and improve its resistance for decay. A typical comparison of grinding energy required for untreated and torrefied wood is illustrated in Fig. 2. This comparison clearly indicates the important role torrefaction can play in reducing the grinding energy of biomass. Torrefied biomass also has higher mass density and it is resistant to water and biological decay. These parameters help the transportation and storage of biomass. The positive features of torrified biomass for gasification are given in Table 7.

3.2 Gasification

For fossil fuel, the gasification technology is very mature and commercialized. Numerous gasifier technologies are available and they are well described in the literature [14]. Earlier commercial gasifiers tend to be low pressure gasifiers operating

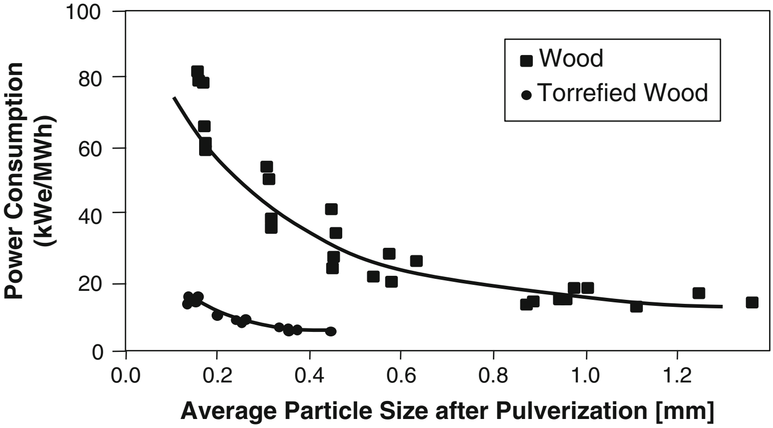


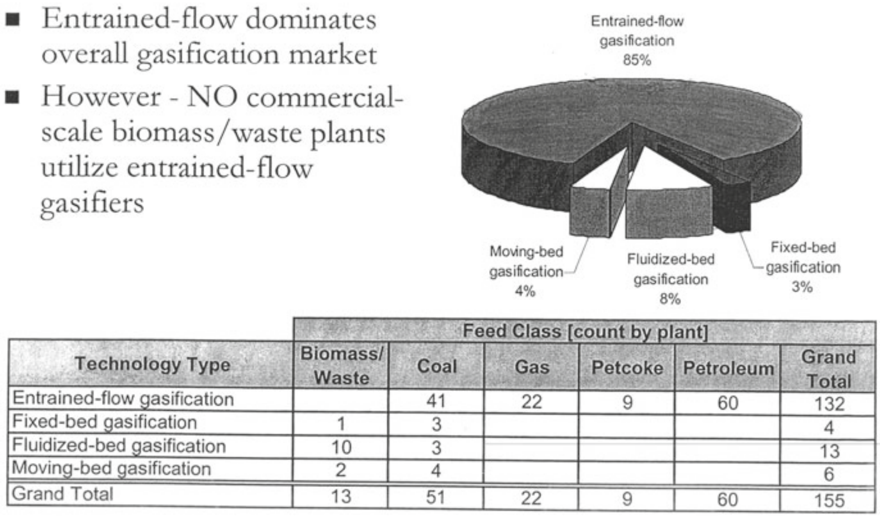
Fig. 2 Power consumption for size reduction: wood vs. torrefied wood [31–35]

Table 7 Positive features of torrefied biomass for gasification and other applications [32–35]

Torrefied product
Has lower moisture content and higher heating value
Is easy to store and transport
Is hydrophobic; does not gain humidity in storage and transportation
Is less susceptible to fungal attack
Is easy to burn, forms less smoke and ignites faster
Significantly conserves the chemical energy in biomass
Has heating value (11,000 Btu/lb) that compares well with coal (12,000 Btu/lb)
Generates electricity with a similar efficiency with that of coal (35% fuel to electricity) and considerably higher than that of untreated biomass (23% fuel to electricity)
Has grindability similar to that of coal
Requires grinding energy 7.5–15 times less than that for untreated biomass for the same particle size
Has mill capacity 2–6.5 times higher compared to untreated biomass
Possess better fluidization properties in the gasifiers
Is suitable for various applications in heating, fuel, steel, and new materials manufacturing industries

with a varying temperature to obtain producer gas with different levels of methane, carbon monoxide, hydrogen, carbon dioxide, and water with other small levels of hydrocarbons and impurities. High, medium, and low Btu gases produced by the gasifier depend on the level of methane in the producer gas. Generally, gasifier either uses air or oxygen. However, in recent years other gaseous carriers such as steam, hydrogen, and carbon dioxide have also been examined. The main purpose has been to improve energy efficiency, conversion, and an adjustment of the final composition of the producer gas. A notable effort on hydrogasification is being carried out at University of California at Riverside [36].

In recent years, high pressure gasifiers have also been tested and preferred. Some efforts have also been made to examine gasification under supercritical conditions.



- Entrained-flow dominates overall gasification market
- However - NO commercial-scale biomass/waste plants utilize entrained-flow gasifiers

Technology Type	Feed Class [count by plant]					
	Biomass/ Waste	Coal	Gas	Petcoke	Petroleum	Grand Total
Entrained-flow gasification		41	22	9	60	132
Fixed-bed gasification	1	3				4
Fluidized-bed gasification	10	3				13
Moving-bed gasification	2	4				6
Grand Total	13	51	22	9	60	155

Fig. 3 Overview of commercial biomass gasification experience: 2004 world gasification survey [38, 39]

Both water and carbon dioxide have been used as supercritical media. These conditions, in general, reduce the required temperature for gasification and it also alters the composition of the producer gas (for example, with super critical water, more hydrogen and carbon dioxide are produced). A good review of gasification in supercritical water has been given by Guo et al. [37].

Numerous reactor technologies for the gasifier have also been tested. Earlier studies used fluidized bed (both homogeneous and turbulent), fixed bed, moving bed, and circulating fluidized bed (CFB) technologies. The CFB was popular because it allowed a better control of the residence time of feed stock within the gasifier. More recently, entrained bed gasifier (or even fast fluidized or transport bed) is used and this technology is recommended for new gasification processes. An overview of commercial gasification reactor technology that is being practiced is illustrated in Fig. 3 [38, 39]. It is clear from this figure that the entrained flow gasifier dominates the commercial market and it should be used for the future gasification of biomass. The entrained bed allows a small residence time with very little backmixing of solid particles. This type of reactor dynamics allows a better modeling and scale-up capability for such a reactor. The entrained bed reactor can also be circulating bed in order to maximize the residence time of the feedstock. Significant research on the design of gasifier internals has also been carried out to improve energy efficiency, reduce formation of harmful gaseous impurities, and reduce or better handle the slag formation within the reactor.

Most gasifiers are operated with dry feed, although GE has developed gasification technology for the slurry feed. Unlike for coal, dry feeding of biomass, particularly

Table 8 Product compositions and applications for various types of reforming reactions [42]

Reforming reaction	H_2/CO	Possible application
Dry reforming	1 or less	Polycarbonates, oxo-alcohol, formaldehyde, iron ore reduction
Partial oxidation	~2	Methanol, FT synthesis
Steam reforming and WGS reaction	>3	H_2 production, NH_3 synthesis

in the pressurized gasifier is a challenging problem. Several devices have been developed (e.g., Stamet) to effectively feed dry biomass in the gasifier. In general, coal gasification is operated at a higher temperature than biomass gasification. This is because biomass is more reactive and easy to thermally decompose. For FT application, a gasifier needs to produce syngas (carbon dioxide and hydrogen) as pure as possible. This is generally achieved by increasing the temperature of the gasifier (greater than 1,200°C). For biomass, a pressurized oxygen-blown entrained flow gasifier is preferred. This technology has been identified as an optimum technology for biosyngas production as it has the advantages of (a) high efficiency of biosyngas production [40], (b) fuel flexibility for all types of biomass, e.g., wood, straw and grassy materials, and coal with possibility to use coal as backup fuel, and (c) suitability for scales of several hundreds to a few thousand megawatt [41]. As discussed earlier, biomass requires significant pretreatment to allow stable feeding to the gasifier without excessive inert gas consumption. Torrefaction is one of the most promising routes, as it has efficiency up to 97% and torrefied biomass can be handled and fed to the gasifier with existing coal infrastructure. Entrained flow gasification for coal is a well established and commercial technology which can be readily adapted for biomass.

In order to get the right composition of syngas and removing methane from the exit gases, the gasifier is often followed by a reformer. The reformer adjusts the syngas composition that is most desirable for FT, methanol, or other syntheses. The typical H_2/CO ratios required for various end uses are described in Table 8. As shown, the nature of reforming process required depends on the end use of the syngas.

3.3 Gas Cleaning and Conditioning

The raw syngas from the gasifier needs significant cleaning and conditioning and treating before it is suitable for subsequent catalytic synthesis. A typical composition of the raw biosyngas from an air-blown CFB gasifier is given in Table 9. The syngas contains H_2/CO ratio of 0.9 and it makes up only 34 vol.% corresponding to 48.9% of chemical energy. The remainder of energy is mainly contained in CH_4, C_2H_4, and benzene (total of 44.4%). As mentioned before, this can be converted to CO and H_2 by appropriate reforming process. The major gas cleaning issue is the presence of 7 g/m^3 of tars in the gas. Tars are condensable organic compounds with boiling points

Table 9 Typical biosyngas composition for gasification of wood (15% moisture) at 850°C in an atmospheric air-blown CFB gasifier [43, 44]

Main components	Vol. %, dry	Impurities	mg/m^3
CO	18	NH_3, HCl, H_2S	2,480
H_2	16	All COS, CS_2, HCN, HBr	<25
CO_2	16	Dust, soot, ash	2,000
H_2O (relative to dry gas)	13		
N_2	42	*Tar classes*	
CH_4	5.5	Class 1 (unidentified)	330
Ethane, ethylene, acetylene	1.85	Class 2 (heteroatoms, phenols)	510
Benzene, toluene, xylene (BTX)	0.53	Class 3 (1 ring excl. BTX)	370
Sum of tars	0.12	Class 4 (2,3 rings, naphthalene)	7,550
Total	100	Class 5 (> or equal 4 ring)	650

between 80 and 350°C. When the temperature in the system decreases below 350°C, tars start condensing resulting in fouling and ultimately failing of the system. Typical inorganic biomass impurities are NH_3, HCl, and H_2S and in minor quantities COS, CS_2, HCN, and volatile metals. Also, 2 g/m^3 of solids are present in raw biosyngas.

A typical gas conditioning lineup comprises gas cooling, water gas shift (or other reforming), CO_2 removal, and impurities removal (e.g., H_2S, COS, HCN, volatile metals). Cooling can be achieved with a cooler or a water quench. While a cooler can utilize latent heat in the gas, for biomass there is an increased risk of fouling due to relative high alkaline and chloride concentrations compared with coal. In a gasifier using water quench, fouling problems are avoided. Except for gas cooling, there is a great deal of similarity in biosyngas conditioning and the treating of fossil fuel-based syngas. Thus, biosyngas can be cleaned using the available technologies for commercial coal to liquid operations. There are no biomass specific impurities that require a totally different gas cleaning approach [40].

In commercial FT operation, catalysts are replaced or regenerated after a certain operational period. The level of gas cleaning is a matter of economics between the cost of catalyst regeneration and the cost of cleaning up front. This economics may depend on the nature of FT synthesis and the catalyst. As a rule of thumb, a maximum value of 1 ppm V may be used for the sum of the nitrogen-containing ($NH_3 + HCN$) and sulfur-containing ($H_2S + COS + CS_2$) compounds. For the halides (HCl + HBr + HF) and alkaline metals, a lower level of 10 ppb V should be targeted. There are no limits regarding the poisoning of the catalysts by the tars. For FT synthesis, since gas is compressed to 25–60 atm pressure, the concentration of organic compounds must be below the dew point at FT pressure so as to avoid condensation of tars which can poison the catalyst and foul up the entire system. For thiophene and pyridine, the concentrations should be below ppmV level since they poison the catalysts. Solids should be removed completely as they foul the system and obstruct the operation of the fixed bed reactor. For H_2, CO, CO_2, CH_4, N_2, paraffins such as ethane and propane, and olefins such as ethylene and propene there are no standards. While hydrocarbons can be further reduced to CO and H_2 by reforming, their small concentrations do not affect the operation of the FT reactor. Often BTX (benzene, toluene, and xylene) are used as guidelines for gas cleaning.

3.4 FT Reactor

FT reactor can be either a fixed bed reactor or a slurry bed reactor. In earlier studies and commercialization, fixed bed reactor technology was extensively used. Since FT process is exothermic, a careful control of heat and mass transfer is very important for CO conversion and catalyst selectivity and stability. In the fixed bed reactor, special efforts have been made to design the reactor internals to remove the heat and control the reactor temperature. More recently, slurry bed reactor is preferred because it offers distinct advantages for the control of both mass and heat transfer problems that may affect the reactor performance. Slurry bed reactor also allows more flexibility in the use of the catalyst particle size. For coal and petroleum derived syngas, commercial FT reactors are being operated by Shell, Exxon, Sasol, Syntroleum among others all over the world. Shell GTL PEARL project in Qatar produces 70,000 bbld (barrels per day). Shell also has a smaller commercial plant in Bintulu, Malaysia which produces 14,700 bbld. Syntroleum operates FT process in Australia. Sasol-QP GTL ORYX-1 project in South Africa produces 34,000 Bbld. These and many other commercial technologies can be readily used for the FT process that uses biosyngas. The size of FT process will depend on the size of the gasifier for an integrated process. For example, a BTL (biomass to liquid) plant producing 2,100 Bbld will require a gasifier producing 250 MWth [38].

While existing commercial technology for GTL and CTL can be used for BTL, the scale of BTL plant is going to be important. Unlike, coal and natural gas, biomass is difficult to transport and store, and the cost of feed preparation of biomass can become an important factor in the scale of BTL process. This issue has been briefly discussed later in the economy of scale of BTL operation. Since FT process is oblivious to how syngas is produced (as long as its composition is not significantly varied), gasification technology is the key to the integration of GTL, CTL, or BTL process. In order to take advantage of the economy of scale, significant efforts are being made to examine CBTL (mixture of coal and biomass to liquid) process. As discussed later, this process offers some distinct advantages over CTL or BTL process.

3.5 Products Separations and Upgrading

The products from the FT reactor are generally separated as gas, liquid, and solid (which may include catalyst for a continuous slurry phase reactor). The off-gases can be recycled back to the gasifier or to FT reactor feed before or after a reforming stage. The catalysts from solids are separated and the remaining solids can also be recycled to the gasifier or a reformer. Portions of hot gas and solids can be used for process heat as well as for the generation of electricity through a downstream combustion process. The main liquid product is then upgraded to produce ASTM standard biodiesel, biogasoline, or biojet fuel using standard refining and hydroprocessing operations. As mentioned earlier, the nature of the liquid produced from FT reactor will depend on the nature of the catalyst, operating conditions, and H_2/CO ratio. The upgrading strategy will, therefore, depend on the nature of the liquid and the desired end-product.

4 An Integrated Process for Biomass to Biodiesel Oil Production via Fischer–Tropsch Synthesis

A schematic of typical integrated BTL process is shown in Fig. 4. Some modifications of this basic process are also being investigated. For example, researchers at University of California, Riverside are examining a process illustrated in Fig. 5. The key modification is the replacement of a conventional gasification by a hydrogasification reactor [36] to produce biosyngas from biomass. In general, various

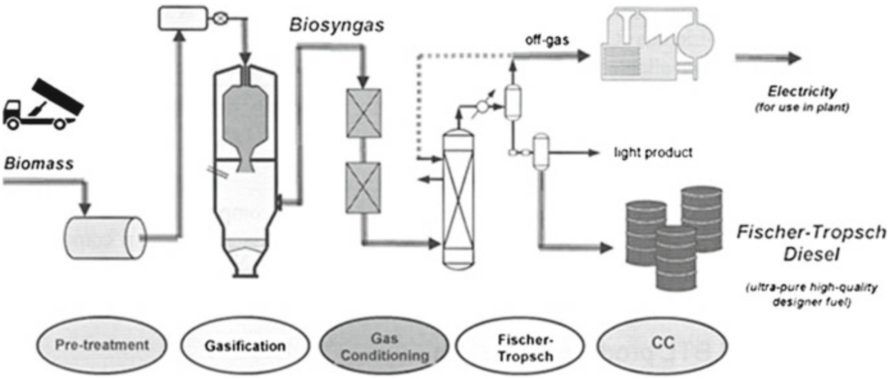


Fig. 4 Schematic lineup of the integrated BTL plant [38]

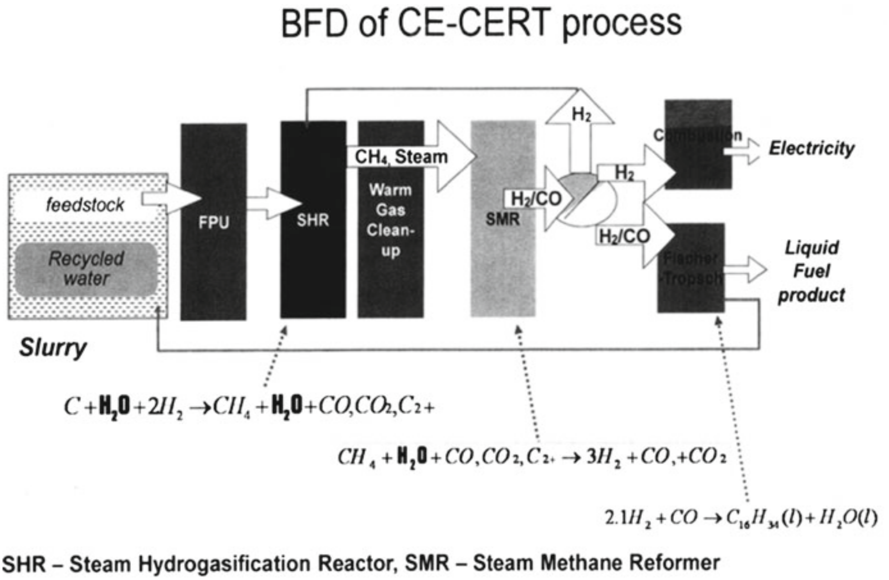

BFD of CE-CERT process
feedstock
Recycled water
Slurry
FPU
SHR
CH_4, Steam
Warm Gas Clean-up
SMR
H_2
H_2/CO
H_2
H_2/CO
Combustion
Electricity
Fischer Tropsch
Liquid Fuel product
$C + H_2O + 2H_2 \rightarrow CH_4 + H_2O + CO, CO_2, C_{2+}$
$CH_4 + H_2O + CO, CO_2, C_{2+} \rightarrow 3H_2 + CO, + CO_2$
$2.1H_2 + CO \rightarrow C_{16}H_{34}(l) + H_2O(l)$
SHR – Steam Hydrogasification Reactor, SMR – Steam Methane Reformer

Fig. 5 A modified integrated BTL process [36]

modifications of an integrated BTL process are possible depending on the use of preferred technologies in basic five elements of an integrated BTL process.

Boerrigter et al. [43] point out that a design of an integrated BTL process depends on whether or not one takes a front-end approach or a back-end approach.

4.1 Front-End Approach

In the front-end approach, the scale of the plant is dependent upon the scale of the gasifier. The principal idea in this approach is that FT liquid, heat and electricity are the desired products. This is generally used for the gasifier of the size 1–100 MWth [45]. In this approach, the off-gases from FT reactor are used to generate heat and electricity in a combined cycle. The fundamental assumptions and other elements that justify this approach are:

1. The gasifier is small and air blown.
2. Once pass through FT reactor operation to avoid accumulations of inert like N_2 (present at 40 vol.% in biosyngas, CO_2, CH_4, and other gaseous C_1 to C_4 FT products).
3. No adjustment of H_2/CO ratio via WGS reaction and CO_2 removal thus reducing the cost of gas conditioning.
4. H_2 concentration is the limiting factor for the conversion of once-through FT synthesis. The unconverted H_2, CO and other hydrocarbons are used to generate heat and electricity. The conversion to liquid is, therefore, low. When the purpose of the tri-generation plant is to improve the production of FT liquid, a shift step is introduced as a part of the overall system. This step allows to maximize the total yield of $H_2 + CO$ in the FT synthesis.
5. The basic gas conditioning system will include the removal of tars and BTX by OLGA unit, the removal of inorganic impurities by wet gas cleaning technique, and the removal of H_2S and remaining trace impurities by ZnO and active carbon filters.

4.2 Back-End Approach

The objective of this approach is to convert feedstock into FT liquid as much as possible. The heat and particularly electricity generations are of secondary importance. This approach requires a large production capacity. Since FT process has a high fixed cost, the economy scale is important to produce FT liquid competitively with other biofuels such as bioethanol, biodiesel, as well as FT liquids derived from fossil fuels [46]. This means gasifiers of the size at least greater than 1,000 MWth are required. Fundamental assumptions and other elements of this approach are:

1. FT off-gas is recycled to the biomass gasifier to achieve maximum syngas conversion. Electricity is produced as a "by-product" from the relatively small recycle bleed stream.
2. The yield of syngas $H_2 + CO$ in the FT feed gas must be as high as possible.

3. Since significant energy remains in CH_4, C_2H_4, BTX, and tar, the process requires tar cracker and shift reactor or a reformer to convert all hydrocarbons into CO and H_2. The increase in feed H_2+CO and increase in their yields result in much higher production of FT liquids and wax and higher overall efficiency of 63.5%.
4. Both gasifier and tar cracker must be oxygen blown to reduce dilution of recycle stream by N_2 and other inert materials.
5. Unlike in the front-end approach, the part of gas conditioning system, CO_2 removal step is essential.

4.3 Economics of an Integrated BTL Process

Boerrigter [43] has studied the economics of BTL plant to produce green biodiesel from biomass using an integrated back-end approach to the plant design. His main conclusions are as follows:

1. Fixed cost for BTL plant is generally 60% higher than the one required for GTL plant of the same size. This is because the requirements of larger air separation unit, 50% more expensive gasifier because of the special solids handling, and the requirement of Rectisol unit for bulk gas cleaning.
2. BTL plants of 1,000–5,000 MWth (size of gasifiers) are optimal.
3. For production below 20,000 Bbld, fixed costs increase very rapidly.
4. The heart of BTL plant is a pressurized oxygen-blown slagging entrained flow gasifier. This technology is identified as an optimum technology for biosyngas production.
5. Torrefaction is the optimum biomass pretreatment technology for the entrained flow gasification.
6. Commercially available technologies can be used for the biosyngas cleaning and conditioning as well as for FT synthesis (both fixed bed and slurry bed).
7. Large-scale facilities are required to take advantage of economy of scale. The increase in transportation cost to provide large-scale facility is less important than decrease in fixed plant costs. For a large-scale process, the diesel generated from BTL plant is competitive with $60/bbl oil price.

5 Future Directions

While significant progress have been made (particularly in Europe) to commercialize BTL plants to generate green fuel, there are several drawbacks in the use of biomass alone as a feedstock for either generation of power or the production of synthetic oil. There is no consistent supply of biomass to operate a commercial sized power or fuel plant. For fuel production, the maximum advantage of the economy of scale requires 500,000 Bbl (barrels)/day of oil production. At the present time, the largest BTL (biomass-to-liquids) plant that may be built will most likely

Table 10 Advantages and disadvantages of use of coal and biomass mixture feed for gasification [50–55]

Advantages	Disadvantages
Economy of scale—smaller biomass plants alone are inefficient and risky	Expensive feed preparation
Lower costs associated with fossil fuel consumption	Complex feed systems for co-gasification
Less CO_2 discharge (see Fig. 2)	Two separate feed injectors, versus single feed injector, may affect the gasifier performance
More stable and reliable feed supply by the mixture	Negative impact of the slagging behavior of the combined ash in the gasifier
Provides more security, less risk	Additional complication to gas cleaning system
More positive public attitude towards use of fossil fuel, renewable fuel, and reliable multisource fuel supply	More tar and oil formation in raw syngas can be a problem depending on the gasification technology

produce 50,000 Bbl/day [47–49]. Also, as discussed earlier, biomass is difficult to store, feed, and transport and requires significant and costly pretreatment. One method that is presently being pursued is to obtain syngas by the gasification of coal and biomass mixture. Once the syngas (with appropriate methane content) from such a mixture is produced, it can be easily used either for power generation or producing a variety of transportation fuel by means of FT synthesis.

The advantages and disadvantages of the co-gasification of coal and biomass mixture are briefly presented in Table 10 [50–55]. As given in this table, co-gasification provides many advantages to the production of the syngas. Pure biomass gasification process is limited to small scale, has high capital (fixed) cost, has lower thermal efficiency, and carries shut down risk. All of these are alleviated by the use of coal. The mixture of coal and biomass provides a stable and reliable feed supply that generates less carbon dioxide. Coal can be considered as the “fly wheel” that allows a continuous plant operation when biomass feedstock is not easily available. Co-gasification reduces the cost associated with fossil fuel consumption although some types of biomass can add significant cost to the overall fuel production. These advantages provide more security and less risks for project financiers than the use of pure biomass and are likely to engender more positive public attitudes towards the use of coal for fuel generation.

Table 10 also presents some disadvantages of co-gasification process. As given in this table, feed preparation and complex feed systems can be expensive. Two separate feed injectors, versus a single feed injector, may affect the gasifier performance. The slagging behavior of combined ash of coal and biomass in the gasifier may have a negative impact [17, 50–55]. The gas cleaning system may have the additional complications due to a mixture of organic and inorganic impurities. Also, depending on the gasification technology, generation of more tar or oil in the product gas may be problematic [34, 36–43].

In summary, when coal and biomass are fed together as a mixture into a gasifier, the process of feeding should be uniform, consistent, and one that allows easy fluidization in any types of gasifier. New short residence time gasifiers prefer dry feeding because it allows maximum flexibility in the allowable operating conditions of the gasifiers. The dry feeding also allows some flexibility in varying the nature of the coal–biomass mixture feedstock. Biomass also needs to be prepared such that it forms a homogenous mixture with coal. A successful CBTL process will truly open up new possibilities for fuel production that can use a wide variety of coal and biomass, our two sources of energy that can clearly replace our demands on oil.

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